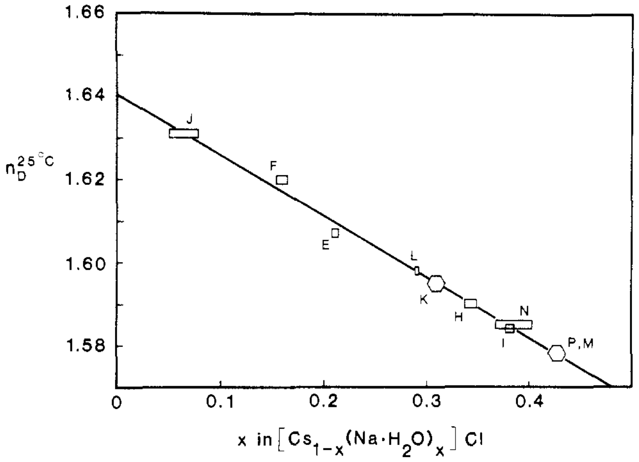

Figure 6. Refractive indices of the crystals in the solid-solution series $[Cs_{1-x}(Na \cdot H_2O)_x]Cl$ (Table II). Letters designate run numbers. Uncertainties are indicated by the size of the rectangles. The solid line represents the least-squares regression of the data. The compositions for K, P, and M (hexagons) were determined from the regression line and from the refractive indices.

solubility data (*1*) and the final solution compositions for runs T, Q, and R. The location of point F is defined by the final solution compositions of runs P and M, in which the solutions coexist with the NC (point X) and the solid solution (point Y). Inside the area EFX, the solution coexists with the incongruently saturated NC as demonstrated by run G.

In the area FGCY, the final solutions, with their compositions along the line FG, coexist with solid solutions along the line CY. The tie lines shown in Figure 3 were experimentally determined as shown in Figure 2. Point G is derived from CsCl solubility data (*6*). The solution-absent area BCX was not investigated in this study.

Conclusion

The solubility relations in the ternary system $NaCl–CsCl–H_2O$ are determined at 25 °C in this study. In addition, a new compound and a new solid-solution series are characterized in terms of chemical composition, crystal structure, and optical properties. Chou and Lee (*1*) have shown that halite solubilities in this system are slightly higher than those reported by Plyushchev et al. (*2*). In the CsCl-rich region, the present solubility data agree with the literature values (*2*) to within 0.5 wt % except that two data points reported by Plyushchev et al. (*2*) for saturated solutions contain 1.4 and 3.6 wt % more H_2O than the present data indicate. Furthermore, the solubility relationships given by Plyushchev et al. (*2*) are considerably revised by introducing a new compound and a new solid solution in the system.

Acknowledgment

The equipment for the refractive index measurements was kindly provided by J. S. Huebner (USGS). Comments from J. L. Haas, Jr., and K. A. McGee of USGS improved the presentation of this paper.

Registry No. $CsCl \cdot 2NaCl \cdot 2H_2O$, 86471-84-3; CsCl, 7647-17-8; NaCl, 7647-14-5.

Literature Cited

(1) Chou, I. M.; Lee, R. D. *J. Chem. Eng. Data*, preceding article in this issue.
(2) Plyushchev, V. E.; Tulinova, V. B.; Kuznetsova, G. P.; Korovin, S. S.; Shipetina, N. S. *J. Inorg. Chem.* (*USSR*) **1957**, *2*, 2654.
(3) Chou, I. M.; Romankiw, L. A.; Evans, H. T.; Konnert, J. A. *EOS* **1982**, *63*, 465.
(4) Evans, H. T.; Konnert, J. A.; Chou, I. M.; Romankiw, L. A. *Am. Crystallogr. Assoc., Program Abstr.* **1982**, *10*, 32.
(5) Ricci, J. E. *J. Am. Chem. Soc.* **1935**, *57*, 805.
(6) Clynne, M. A.; Potter, R. W., II. *J. Chem. Eng. Data* **1979**, *24*, 338.

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Solubility Relations in the Ternary System $NaCl–CsCl–H_2O$ at 1 atm. 3. Solubility Relations at 50 and 75 °C

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Solubility relations in the CsCl-rich region of the ternary system $NaCl–CsCl–H_2O$ were determined at 50 and 75 °C by the isothermal method. The new compound, $CsCl \cdot 2NaCl \cdot 2H_2O$, found at 25 °C in this system is not stable at 50 and 75 °C. However, the solid solutions, $[Cs_{1-x}(Na \cdot H_2O)_x]Cl$, remain stable with x values ranging from 0 to 0.352 at 50 °C and from 0 to 0.325 at 75 °C. By combining the present results with the halite solubility data reported earlier in this series, we have established the solubility relations of the entire system at 50 and 75 °C.

Introduction

Halite solubilities in the system $NaCl–CsCl–H_2O$ from 20 to 100 °C were reported in part 1 of this series (*1*). Solubility relations in this system at 25 °C were given in part 2 (*2*). This paper presents the solubility relations at 50 and 75 °C.

Experimental Section

The isothermal method (*2*) was used in this study. Samples were reacted at 50 and 75 °C for at least 14 and 7 days, respectively, to ensure equilibration (*3*). After each run, solids and solution were separated and analyzed.

Results and Discussion

The solubility data are given in Table I. The bulk compositions reported are accurate to ±0.03 wt %. The final solid

Table I. Solubility Data in the System NaCl-CsCl-H_2O at 50 and 75 °C

run no.	bulk composition, wt %			final composition, wt %									solid phases[d]
				solid[a]			solid[b]			soln[c]			
	NaCl	CsCl	H_2O	NaCl	CsCl	H_2O	NaCl	CsCl	H_2O	NaCl	CsCl	H_2O	
							Temperature = 50 °C						
A-2	9.98	53.00	39.02	15.12[e]	80.22[e]	4.66[e]				8.28[f]	53.54[f]	38.18	h + ss
A-3	8.00	55.91	36.09	13.69	82.09	4.22	13.20	82.73	4.07	7.75	54.77	37.48	ss
A-4	7.30	58.21	34.49	12.66	83.44	3.90	12.10	84.17	3.73	6.99	56.44	36.57	ss
A-5	4.99	62.98	32.04	8.77	88.52	2.70	9.02	88.20	2.78	4.75	60.79	34.46	ss
A-6	2.53	66.87	30.60	4.17	94.54	1.29	4.28	94.40	1.32	2.53	65.25	32.22	ss
							Temperature = 75 °C						
B-2	8.47	59.04	32.49	13.69[e]	82.09[e]	4.22[e]				7.48[f]	59.23[f]	33.29	h + ss
B-3	7.03	60.98	31.99	12.32	83.89	3.80	11.47	85.00	3.54	6.98	60.00	33.02	ss
B-4	5.96	63.06	30.98	10.34	86.47	3.19	10.19	86.67	3.14	5.70	62.00	32.30	ss
B-5	3.97	65.94	30.09	7.57	90.10	2.33	6.81	91.09	2.10	3.93	65.45	30.62	ss

[a] Calculated from x values derived from $n^{25}{}_D$ (Table II). [b] Calculated from x values derived from H_2O-content measurements (Table II). [c] For derivation, see text. [d] h = halite; ss = solid solution $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$. [e] For the solid-solution phase only. [f] Derived from chloride analysis data using the procedures described earlier (*2*).

Table II. Refractive Indices ($n^{25}{}_D$) and Compositions (x in the formula $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$) of Solid Solutions Equilibrated at 50 and 75 °C

run no.	$n^{25}{}_D$ (±0.001)	x^a	x^b
	Temperature = 50 °C		
A-2	1.589	0.352	
A-3	1.593	0.325	0.315
A-4	1.596	0.304	0.293
A-5	1.608	0.222	0.228
A-6	1.624	0.113	0.116
	Temperature = 75 °C		
B-2	1.593	0.325	
B-3	1.597	0.297	0.280
B-4	1.603	0.256	0.253
B-5	1.612	0.195	0.177

[a] Values derived from $n^{25}{}_D$; see text for details. [b] Values derived from H_2O-content measurements; see text for details.

compositions were determined by two independent methods:

(a) refractive indices measurements—The refractive indices of the solid solutions, $[Cs_{1-x}(Na\cdot H_2O)_x]Cl$, were measured and the values for x were calculated from the regression equation established earlier (ref *2*, Figure 6)

$$x = -6.83176n^{25}{}_D + 11.2075. \qquad (1)$$

(b) H_2O-content measurements—The H_2O contents were determined gravimetrically (*2*), and the x values in the solid-solution formula were calculated from the relationship

$$\text{wt \% } H_2O \text{ in solid solution} = (100)(18.015)x/(168.3584 - 91.9006x) \qquad (2)$$

Values for x obtained from both methods are given in Table II. The compositions of solid solutions (in wt %) calculated from these x values are listed in Table I. These two sets of data agree within ±1.11 wt %. Compositions derived from $n^{25}{}_D$ data are preferred as $n^{25}{}_D$ can be determined to ±0.001 whereas the H_2O contents of these samples are small (<5 wt %) and hence difficult to measure accurately. The preferred values are estimated to be accurate to ±1 wt %.

The compositions of the final solutions (Table I) for runs A-2 and B-2 were determined by the chloride titration method (*2*). For the remaining runs, the solution compositions were obtained graphically by using the Schreinemaker residue method, in which the final solution composition lies on the straight line defined by the bulk composition and the final solid composition. The exact location of the final solution composition on this line was defined by the H_2O content of the solution determined

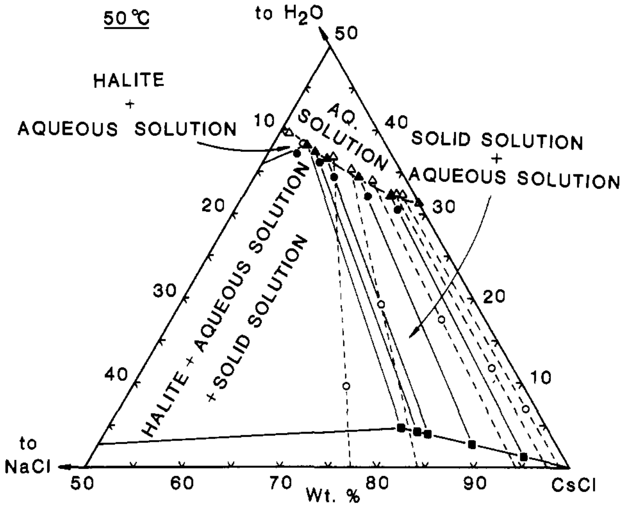

Figure 1. Solubility relations in the CsCl-rich region of the system NaCl–CsCl–H_2O at 50 °C. Solid symbols are from the data listed in Table I. The solid tie lines are defined by the bulk compositions (solid circles) and the final solid compositions (solid squares), which are obtained from $n^{25}{}_D$ measurements. The final solution compositions (solid triangles) are defined by the solid tie lines and the H_2O content of the solution. The open symbols are from Plyushchev et al. (*3*). The dashed tie lines are defined by the bulk compositions (open circles) and the final solution compositions (open triangles). Solid solutions between CsCl and NaCl were suggested (*3*). Their eutonic solution composition is shown by the hexagon.

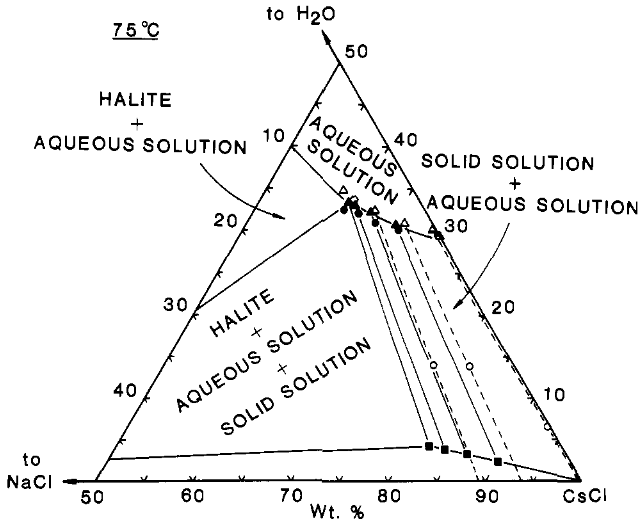

Figure 2. Solubility relations in the CsCl-rich region of the system NaCl–CsCl–H_2O at 75 °C. Symbols are the same as in Figure 1.

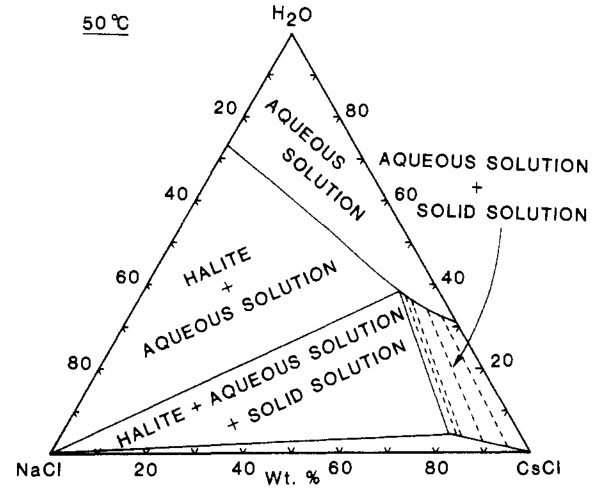

Figure 3. Solubility relations in the system NaCl-CsCl-H_2O at 50 °C. The dashed lines are experimentally determined tie lines (see Figure 1).

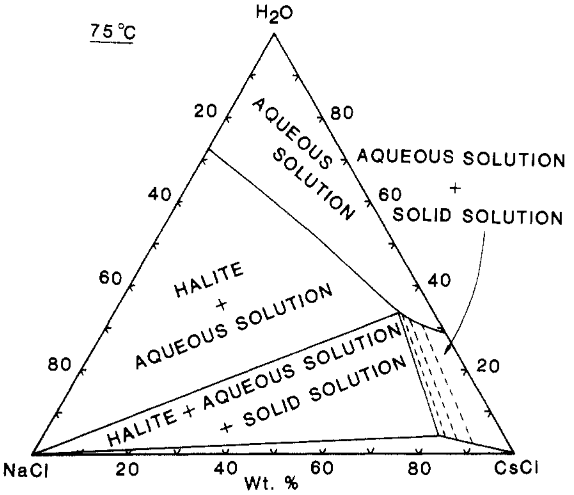

Figure 4. Solubility relations in the system NaCl-CsCl-H_2O at 75 °C. The dashed lines are experimentally determined tie lines (see Figure 2).

gravimetrically (*2*). The reported solution compositions (Table I) are accurate to ±0.3 wt %.

Results are summarized in Figures 1 and 2 (solid symbols and solid lines) for 50 and 75 °C experiments, respectively. The solubilities of CsCl in H_2O are from Clynne and Potter (*4*). Also shown in these figures (open symbols and dashed lines) are the solubility relations given by Plyushchev et al. (*3*). The compositions of their solids were not determined. However, the existence of solid solutions between NaCl and CsCl was proposed. Their solubility data agree with our values to within ±0.5 wt % at 50 °C and within ±0.8 wt % at 75 °C. The orientations of their solid-solution tie lines (dashed lines in Figures 1 and 2) agree very well with ours (solid lines) at 75 °C. However, the agreement at 50 °C is limited to the most CsCl-rich region only. The composition of their eutonic solution (the solution that coexists with two solids) agrees with that of ours to ±0.37 wt % at 50 °C and to ±0.73 wt % at 75 °C.

By combining our results here with the halite solubility data presented earlier (*1*), we were able to determine the solubility relations of the entire system at 50 and 75 °C. These relations are shown in Figures 3 and 4. At these temperatures, the new compound, $CsCl{\cdot}2NaCl{\cdot}2H_2O$, found at 25 °C (*2*) is not stable. However, the solid solutions, $[Cs_{1-x}(Na{\cdot}H_2O)_x]Cl$, remain stable at these temperatures. The maximum values for x are 0.352 at 50 °C and 0.325 at 75 °C, compared with a value of 0.427 at 25 °C (*2*).

Conclusion

The solubility relations in the system NaCl-CsCl-H_2O are determined at 50 and 75 °C. Our solubility data agree very well with the literature values (*3*). However, the relations between the solutions and the coexisting solids reported by Plyushchev et al. (*3*) are modified considerably in this study.

Registry No. Cesium chloride, 7647-17-8; sodium chloride, 7647-14-5.

Literature Cited

(1) Chou, I. M.; Lee, R. D. *J. Chem. Eng. Data*, first of two preceding articles in this issue.
(2) Chou, I. M.; Romankiw, L. A.; Evans, H. T.; Konnert, J. A. *J. Chem. Eng. Data*, second of two preceding articles in this issue.
(3) Plyushchev, V. E.; Tulinova, V. B.; Kuznetsova, G. P.; Korovin, S. S.; Shipetina, N. S. *J. Inorg. Chem.* (*USSR*) **1957**, *2*, 2654.
(4) Clynne, M. A.; Potter, R. W., II. *J. Chem. Eng. Data* **1979**, *24*, 338.

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Vapor–Liquid Equilibria for the Ternary Systems Acetonitrile–2-Butanone–Benzene and Acetonitrile–Methanol–Benzene at 328.15 K

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Isothermal vapor–liquid equilibrium data at 328.15 K are presented for the ternary systems acetonitrile–2-butanone–benzene and acetonitrile–methanol–benzene, and three binary systems: 2-butanone–acetonitrile, 2-butanone–benzene, and acetonitrile–benzene. Experimental data are correlated by the Wilson and UNIQUAC equations and the UNIFAC method.

Introduction

Vapor–liquid equilibrium data at 328.15 K were obtained for the two ternary systems acetonitrile–2-butanone–benzene and acetonitrile–methanol–benzene, and three binary systems: 2-butanone–acetonitrile, 2-butanone–benzene, and acetonitrile–benzene with a Boublik still (*1*). Isothermal vapor–liquid equilibrium data for the binary systems have been published by several investigators: 2-butanone–acetonitrile (*2*); 2-buta-

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